drop across this resistance is impressed between the grid and filament of the thyratron tube. As soon as this exceeds any predetermined value (that is, as soon as the temperature exceeds a predetermined value), the thyratron tube is turned on. This in turn shuts off the supply of heat from the furnace. The furnace then cools down, the photo current decreases, and the thyratron tube is turned off and the cycle repeated.

The control mechanism may be varied to suit the individual needs. In the case just described, one thyratron tube was used and the control was limited to keeping the temperature below a certain maximum. By the use of two tubes, both upper and lower limits may be set.

At the present time vacuum photoelectric tubes can be depended on to maintain constant current to within about 10 per cent. Since the light output varies so rapidly with temperature, a change of 10 per cent in the radiation from a black body at 1500° C. would correspond to a change in temperature of about 10° C. That is, a 10 per cent variation in photoelectric tube sensitivity will not cause a greater error than 10° C. (at 1500° C.) in the calibration of the apparatus.

Changes in the amplifier tube during life do not affect the accuracy of the measurements, since these changes do not affect the slope of the amplifier characteristic, but only cause a lateral displacement. This only affects the zero of the scale, which is always adjusted by means of the grid bias rheostat before the start of each run.

Constancy in line voltage greatly increases the accuracy of the readings. If the instrument indicates a temperature of 1452° C. when the line voltage is 120, it will read 1440° C. at a line voltage of 115, and 1422° C. at 110.

The complete apparatus is shown in Figure 4.

Some of the advantages of photoelectric tube pyrometry are that the method can be applied to high temperatures or to atmospheres which would be deleterious to thermocouples or resistance thermometers. None of the working parts is placed within the furnace, and the apparatus may be placed at some distance from the furnace. The apparatus functions instantaneously and contains no moving parts. It can be used to control the temperature of any part of the furnace or of the charge itself. The chief advantage, however, lies in the fact that it furnishes a reliable method for automatically controlling furnace temperatures.

Higher Alcohols Formed from Carbon Monoxide and Hydrogen[1,2]

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The following higher alcohols have been identified as products of the high-pressure alcohol synthesis operated by the Du Pont Ammonia Corporation: primary alcohols—*n*-propanol, isobutanol, 2-methyl-1-butanol, 2-methyl-1-pentanol, 2,4-dimethyl-1-pentanol, 4-methyl-1-hexanol; secondary alcohols—isopropanol, 3-methyl-2-butanol, and 2,4-dimethyl-3-pentanol.

Strong evidence was obtained for the presence of: primary alcohols—2,4-dimethyl-1-hexanol and 4- or 5-methyl-1-heptanol; secondary alcohols—3-pentanol, 2-pentanol, and 2-methyl-3-pentanol.

Three simple assumptions are presented, describing a mechanism of synthesis which accounts for the compounds listed, and which explains the absence of substances not identified: (1) Higher alcohols result from intermolecular dehydration of two lower alcohol molecules. (2) Dehydration involves removal of hydrogen either from the hydroxylated carbon atom, thus producing secondary alcohols (except in the case of methanol), or from the carbon adjacent, producing primary alcohols. (3) Hydrogen separates most readily from a CH_2 group, with more difficulty from a CH_3 group, and not at all from a CH group.

THE complexity of the higher-boiling fractions of the product of high-pressure synthesis from hydrogen and carbon monoxide has long been recognized. As a result of large-scale manufacture of methanol and higher alcohols by the Du Pont Ammonia Corporation, ample quantities of well-defined fractions have been produced to make possible the identification of a number of individual compounds, which are described in Part I of this paper. In Part II a number of suggestions are made as to a possible mechanism for their formation.

PART I—IDENTIFICATION OF HIGHER ALCOHOLS

Early work on the fractions boiling above methanol demonstrated the presence of small traces of ethyl alcohol with relatively large amounts of *n*-propanol, isobutanol, and 2-methyl-1-butanol. It was recognized that still higher fractions might well contain isomeric alcohols as well as various compounds other than alcohols, such as hydrocarbons, ethers, aldehydes, or esters. It was further recognized that there might be secondary or tertiary alcohols as well as primary alcohols. Preliminary analytical work demonstrated the absence of aldehydes and esters. It was therefore planned to study first the primary alcohols which were to be isolated by treatment of the mixture with phthalic anhydride in refluxing benzene solution, a process which would esterify the primary alcohols and leave unchanged the secondary alcohols, tertiary alcohols, and other constituents which could be separated by distillation for further study. The primary alcohols were then to be set free by saponification and fractionally distilled.

Raw Materials—The crude higher-alcohol mixture was obtained from the Belle plant of the Du Pont Ammonia Corporation. It boiled from 85° to 162° C. A preliminary fractional distillation showed the distribution as given in Table I.

Separation of Primary Alcohols—The procedure found to be satisfactory for separating the primary alcohols from the other material was as follows:

A benzene solution of the crude fraction and approximately an equimolar proportion of phthalic anhydride (calculated according to the boiling range of the crude being treated) was heated overnight on a steam bath. The solution was then cooled

[1] Received August 4, 1931.

[2] Contribution No. 70 from the Experimental Station of E. I. du Pont de Nemours & Company, Wilmington, Del.

to 5–10° C. to precipitate unchanged phthalic anhydride, which was filtered off and washed twice by resludging with benzene.

The filtrate, which contained the monophthalate of the primary alcohols, was made very slightly alkaline with 10 per cent sodium hydroxide. The upper layer which separated contained unesterified material with some dissolved sodium monoalkyl phthalate. After being washed with water twice, it was dried by distilling off part of the benzene, and treated again with phthalic anhydride until practically nothing more could be esterified. This usually required about four treatments. The benzene was then removed by distillation, leaving a residue of the material not primary alcohol.

The lower or aqueous layer which contained the sodium alkyl phthalate was freed from dissolved benzene and unesterified oil by steam distillation from the slightly acid solution. The ester was not hydrolyzed to any extent unless the distillation was unduly prolonged. The oil layer from the distillate was combined with the benzene layer mentioned above.

The monophthalates of the primary alcohols were saponified by heating with an excess of sodium hydroxide. The liberated alcohols were removed by steam distillation.

After treating several gallons of the crude alcohol by the above procedure, it was found that 48.5 per cent by weight consisted of primary alcohols, while 51.5 per cent was not esterified by phthalic anhydride in refluxing benzene, and must therefore be other than primary alcohols.

Table I—Fractional Distillation of Crude Higher-Alcohol Mixture

Boiling Range ° C.	Weight %
85–129	3.5
129–132	25.1
132–138	18.7
138–142	11.1
142–147	20.1
147–152	5.9
152–158	3.1
158–162	5.9
162–165	0.3
165–170	1.0
170–175	1.0
175–180	1.4
180–185	0.3
185–191	1.0
191–196	0.3
Residue	0.2
	98.9

Identification of Primary Alcohols

The mixture of primary alcohols was submitted to careful fractional distillation, using a 4-foot (1.2-meter) glass column 5/8 inch (1.6 cm.) in diameter, packed with small pieces of crystal silicon carbide. The column was enclosed in a glass jacket, wrapped with a nichrome heating wire, and lagged. The head of the column was fitted with a thermometer, which was placed in the axis of the column, and a short horizontal vapor take-off set slightly above the bulb of the thermometer. This was connected to a vertical reflux condenser extending upwards and a capillary draw-off and stopcock extending downwards. Thus the entire distillate was condensed and returned to the head of the column, except for the amount drawn off through the stopcock. The entire set-up was enclosed in a wooden closet with a glass door. By proper adjustment of the heat supplied to flask and column, and of the amount of distillate removed, very close fractionation was obtained. The rate of distillation was about one drop per second with a ten-to-one reflux ratio.

It became evident at once that the primary alcohol portion, in contrast to the crude mixture before treatment with phthalic anhydride, could be separated into definite constant-boiling fractions by careful fractional distillation. The constant-boiling fractions comprised 86 per cent of the total; the intermediate fractions showed no indication of the presence of single constituents.

As can be seen by reference to Table II, four of the six constant-boiling fractions were definitely identified by comparison with synthetic samples of known constitution. Formulas have been suggested for the other two compounds, based on theoretical considerations presented in the second part of this paper.

The substances actually identified are: 2-methyl-1-butanol; 2-methyl-1-pentanol; 2,4-dimethyl-1-pentanol; and 4-methyl-1-hexanol.

The formulas suggested for the other two primary alcohols are: 2,4-dimethyl-1-hexanol; and 4- or 5-methyl-1-heptanol.

Identification of Material Not Esterified by Phthalic Anhydride

The oil freed from primary alcohols had the characteristic camphoraceous odor of the original crudes. However, the primary alcohols themselves had the somewhat musty odor characteristic of such compounds.

The usual qualitative tests showed the oil to be free from acids, esters, ketones, and olefins. Its solubility in cold concentrated sulfuric acid indicated the absence of hydrocarbons. It reacted slowly with sodium to give hydrogen, and rapidly with acetyl chloride to give an ester and not an alkyl halide. Denigès' test (*3*) for tertiary alcohols was negative. These tests showed that the oil contained saturated secondary alcohols.

Since only secondary alcohols seemed to be present in the mixture, it was subjected to a careful fractional distillation. The results are shown in Table III.

Table III—Fractional Distillation of Secondary Alcohols

Cut	Boiling Range ° C.	Weight of Higher Alcohols %
1	Below 120	5.3
2	120–134	3.0
3	134–139	35.3
4	139–144	3.0
5	144–153	0.8
6	153–160	0.6
7	160–161	0.5
8	161–165	0.9
9	165–169	1.1
10	169–179	0.5
		51.0

From the distillation curve plotted from the above data, it was evident that no separation into individual compounds was being obtained except in cut 3 where a large fraction of quite constant boiling range was separated. Careful refractionation gave a substance boiling at 137–138° C., which seemed to be a pure compound. Analysis showed it to be a heptyl alcohol. Its molecular weight was 113, compared to the calculated value of 116. Microcombustion analysis showed 73.3 per cent carbon and 13.1 per cent hydrogen, compared to calculated values of 72.4 per cent and 13.8 per

Table II—Properties of Primary Alcohols

Substance	Boiling Point Found ° C.	Boiling Point From literature ° C.	Neutral Equiv. of 3-Nitrophthalate Found	Neutral Equiv. of 3-Nitrophthalate Calcd.	Melting Point of 3-Nitrophthalate Of substance ° C.	Melting Point of 3-Nitrophthalate Of known material ° C.	Mixed Melting Point ° C.	Weight of Higher Alcohol %
2-methyl-1-butanol	128–30	129.5	296	295	156	157	156.7	17.3
2-methyl-1-pentanol	145–7	146.5	300	295	141	145	143	16.6
2,4-dimethyl-1-pentanol	153–8	159–161	310	309	152–3	154–5	152–3	2.3
4-methyl-1-hexanol	162–4	165	312	309	140	144	141	3.3
2,4-dimethyl-1-hexanol[a]	173–5	175–80[b]	321	323	132	...	...	1.0
4- or 5-methyl-1-heptanol[a]	180–3	182.7	327	323	133	...	...	0.3

[a] See Part II for justification of these suggested formulas.
[b] Estimated by analogy: the compound has not hitherto been described in the literature.

cent, respectively. The acetate, prepared by means of acetyl chloride, boiled at 160–161° C. and had a saponification number of 355.6, equivalent to a molecular weight of 157 (calculated 158).

The identity of the substance was proved by comparison with synthetic 2,4-dimethyl-3-pentanol (diisopropyl carbinol). The synthetic material boiled at 139° C. and formed an acetate boiling at 160–161° C. Its 3-nitrophthalate melted at 150°, while the same derivative from the unknown melted at 152° C. The mixed melting point was 151° C., proving the identity of the materials.

Since the fractional distillation of the higher-boiling secondary alcohols showed that individual compounds cannot be separated in this way, no other individual secondary alcohols were identified in these fractions.

When it was recognized that the higher-boiling fractions of the alcohol crudes contained secondary alcohols, it appeared quite likely that the lower-boiling fractions would also contain secondary alcohols.

Because of the low boiling points of the water binaries of these compounds and because of the method of separation used in the plant, the oil under investigation could not be expected to contain any of the secondary alcohols below the heptyl alcohols. A rather superficial study was therefore made of some of the lower fractions from the Belle Plant. There seems to be little doubt of the presence of the following substances:

Isopropanol was not isolated but was identified by oxidation to acetone. It was present in very small amounts, as would be expected, since it would undergo further condensation very readily.

3-Methyl-2-butanol, boiling point 114° C., was definitely identified by comparison with synthetic material (3-nitrophthalate, melting point 127° C.; 3-nitrophthalate, from Eastman's product, melting point 124° C.; mixed melting point 124–7° C.).

Fractionation of other secondary alcohol materials gave constant-boiling cuts at 114°, 117°, 119°, and 127° C., corresponding, respectively, to 3-methyl-2-butanol, 3-pentanol, 2-pentanol, and 2-methyl-3-pentanol. Dehydrogenation of a mixture of these fractions by means of a copper catalyst gave a ketone mixture which, on fractionation, showed constant-boiling cuts at 102° C. (corresponding to both methyl isopropyl ketone and diethyl ketone), and at 115° C. (corresponding to ethyl isopropyl ketone). The presence of 2-methyl butyraldehyde from some 2-methyl-1-butanol left in the mixture obscured the presence of methyl isopropyl ketone which boils at 92° C. Examination of the fractionation curve of the alcohols and ketones leaves little doubt of the presence of the alcohols mentioned.

PART II—SUGGESTED MECHANISM FOR FORMATION OF HIGHER ALCOHOLS

Review of Previous Investigations

Various investigators have recognized the production of higher alcohols, aldehydes, ketones, esters, and hydrocarbons during methanol synthesis. A comprehensive review has recently been published by Ellis (*4*). Fischer and Tropsch (*5*), in their early work on synthol, isolated and identified methanol, ethyl alcohol, *n*-propanol, acetaldehyde, propionaldehyde, acetone, methyl ethyl ketone, diethyl ketone, and methyl *n*-propyl ketone, as well as esters and hydrocarbons. These investigators have suggested that the higher alcohols are formed by reduction of aldehydes, which result from the reduction of acids, which in their turn result from the addition of carbon monoxide to an alcohol containing one less carbon atom. The ketones were supposed to result from loss of water and carbon dioxide from two molecules of fatty acids. It will be noted that the addition of carbon monoxide to an alcohol can result in the formation of straight-chain fatty acids only, so that the primary alcohols would also be normal.

Patart (*10*) states that (along with methanol) ethyl, propyl, butyl, and other alcohols through the octyl alcohols are obtained, together with ketones (representing dehydration products of secondary alcohols) and aldehydes (similarly produced from primary alcohols).

Morgan (*8*) presents a series of equations showing how higher alcohols might be synthesized through aldol condensations, starting with formaldehyde. Two molecules of formaldehyde would condense to give $CH_2OH{\cdot}CHO$, which would be hydrogenated to give acetaldehyde and water. Then acetaldehyde would be reduced to ethyl alcohol or would condense with formaldehyde or acetaldehyde to give hydroxy aldehydes of higher molecular weight, which would in turn be dehydrated and reduced. It will be noted again that straight-chain alcohols should be formed, especially *n*-butanol, from two molecules of acetaldehyde. Provision is made for the production of branched-chain alcohols through a condensation involving two molecules of formaldehyde and one of acetaldehyde to give the product $(H_2COH)_2CHCHO$, which, after dehydration and reduction, would give isobutanol.

Progressive dehydration has been proposed as a mechanism for the formation of higher alcohols by Frolich (*6*), who suggests that the methyl ether observed by Brown and Galloway (*2*) undoubtedly represents an intermediate step in the production of its isomer, ethyl alcohol. In this way two molecules of methanol are dehydrated to form methyl ether, which rearranges to form ethyl alcohol. According to this mechanism, the next step in the process would be the formation of ethyl methyl ether from methanol and ethyl alcohol. This substance would rearrange to *n*-propanol. If diethyl ether were to be formed, it would rearrange presumably to ethyl methyl carbinol (*sec*-butanol) rather than to *n*-butanol. Thus primary alcohols would result from rearrangement of methyl ethers only. Frolich also points out that one would expect the aldehydes to be converted to esters by addition and rearrangement; esters have actually been identified in higher alcohol crudes.

A similar condensation of aldehydes to higher alcohols and esters has been described by Adkins, Kinsey, and Folkers (*1*), who give a series of aldol condensations and hydrogenations to explain the formation of ethyl alcohol, ethyl acetate, ethyl butyrate, ethyl caproate, and higher esters, alcohols, and ethers from the catalytic condensation of acetaldehyde in the presence of hydrogen. Under the conditions of the experiment the esters have predominated over the higher alcohols.

The direct condensation of alcohols to higher alcohols by means of methanol catalysts has been described by Neumann (*9*), who has obtained butyl alcohol from ethyl alcohol, 2-methyl-1-pentanol from propyl alcohol, methyl isobutyl carbinol from isopropanol, and a mixture of methyl isobutyl carbinol and methyl *n*-propyl carbinol from ethyl alcohol and isopropanol together. He proposes a mechanism involving aldol condensations. Aldehydes and ketones are therefore intermediates in the formation of the higher alcohols.

The formation of these same higher alcohols by heating the lower alcohols with alkali has been reported by several investigators. Guerbet (*7*) reported that methanol does not condense, but that higher alcohols react with increasing ease. The structure of the product given by Guerbet and by Weizmann and Garrard (*11*) indicates that the condensation always involves a hydrogen atom attached to the beta-carbon atom, giving a series of branched-chain primary alcohols. It is unlikely that these condensations go through the aldehyde stage under the experimental conditions, so that a direct dehydration involving the hydroxyl group of

one alcohol and a hydrogen atom on the beta-carbon atom of the other alcohol is indicated.

The direct dehydration mechanism proposed by Guerbet offers a simple and satisfactory explanation of the formation of *n*-propanol, isobutanol, and 2-methyl-1-butanol, which had been identified in the Du Pont Ammonia by-product alcohols before this investigation was begun. The presence of esters has not been demonstrated. The low-boiling fractions contain traces of aldehydes and ketones which have been looked upon as dehydrogenation products of the alcohols rather than as residual intermediates produced by aldol condensation. Furthermore, the absence of *n*-butanol speaks against the aldol mechanism. The small amounts of saturated and unsaturated hydrocarbons which have been identified in the low-boiling fractions can similarly be explained as dehydration products of the alcohols. Compared to the higher alcohols themselves, all of these other materials are found only in traces.

Formation of Primary Alcohols

In order to investigate the dehydration mechanism, the following ten reactions were written, representing all that can occur between methanol, ethyl alcohol, *n*-propanol, isobutanol, and 2-methyl-1-butanol, through which there will be produced primary alcohols by condensation either on the methyl group of methanol or on the beta-carbon atom of alcohols above methanol.

$$CH_3OH + HCH_2OH \longrightarrow CH_3CH_2OH \quad (1)$$
(ethyl alcohol)

$$CH_3OH + HCH_2CH_2OH \longrightarrow CH_3CH_2CH_2OH \quad (2)$$
(*n*-propanol)

$$CH_3CH_2OH + HCH_2OH \longrightarrow CH_3CH_2CH_2OH \quad (3)$$
(*n*-propanol)

$$CH_3OH + CH_3HCHCH_2OH \longrightarrow CH_3CH(CH_3)CH_2OH \quad (4)$$
(isobutanol)

$$CH_3CH_2CH_2OH + HCH_2OH \longrightarrow CH_3CH_2CH_2CH_2OH \quad (5)$$
(*n*-butanol)

$$CH_3CH_2OH + HCH_2CH_2OH \longrightarrow CH_3CH_2CH_2CH_2OH \quad (6)$$
(*n*-butanol)

$$CH_3OH + CH_3CH(CH_3)CH_2OH \longrightarrow (CH_3)_3CCH_2OH \quad (7)$$
(tertiary butyl carbinol)

$$CH_3CH(CH_3)CH_2OH + HCH_2OH \longrightarrow CH_3CH(CH_3)CH_2CH_2OH \quad (8)$$
(isoamyl alcohol)

$$CH_3CH_2OH + CH_3HCHCH_2OH \longrightarrow CH_3CH(C_2H_5)CH_2OH \quad (9)$$
(2-methyl-1-butanol)

$$CH_3CH_2CH_2OH + HCH_2CH_2OH \longrightarrow CH_3CH_2CH_2CH_2CH_2OH \quad (10)$$
(*n*-amyl alcohol)

The first reaction is required to start the series. The identification of very small amounts of ethyl alcohol in the lower-boiling fractions proves that it actually may take place. Then either Reaction 2 or 3 follows to give *n*-propanol. Reaction 3, however, seems less likely than Reaction 2, since the products of Reactions 5 and 8, which are analogous to 3 in the removal of a hydrogen atom from methanol, have not been identified in the crude. The failure of these reactions indicates that a hydrogen from methanol is not easily removed. Furthermore, since the products of Reactions 6 and 10 have not been identified, it seems that a hydrogen is not easily removed from a CH_3 group at the end of a chain. Failure of Reaction 7 indicates that hydrogen is not removed from a CH group.

It thus appears that the only reactions to occur are (1), (2) or (3), (4), and (9). The following tentative hypotheses were therefore set up to aid in the investigation of the alcohols above amyl:

(1) Higher primary alcohols are formed by intermolecular dehydration of two lower-alcohol molecules.

(2) Dehydration may involve a hydrogen atom on the carbon atom of methanol (see Reactions 1 and 3), but such a reaction is slow compared to one involving a hydrogen on a beta-carbon atom (occurrence of Reactions 2, 4, and 9, and failure of 5 and 8).

(3) Condensation takes place with difficulty on a CH_3 group (failure of Reactions 6 and 10) and does not take place on a CH group (failure of Reaction 7). Most of the higher alcohols result from a condensation on a CH_2 group.

These hypotheses were then applied to the formation of alcohols above pentyl by writing all of the reactions which could take place in accordance with them between the alcohols, through 2-methyl-1-butanol. For the formation of hexyl alcohols, one may write:

$$CH_3CH_2CH(CH_3)CH_2OH + HCH_2OH \longrightarrow CH_3CH_2CH(CH_3)CH_2CH_2OH \quad (11)$$
(3-methyl-1-pentanol, b. p. 152° C.)

$$CH_3CH(CH_3)CH_2OH + HCH_2CH_2OH \longrightarrow CH_3CH(CH_3)CH_2CH_2CH_2OH \quad (12)$$
(4-methyl-1-pentanol, b. p. 147–148° C.)

$$CH_3CH_2CH_2OH + CH_3HCHCH_2OH \longrightarrow CH_3CH_2CH_2CH(CH_3)CH_2OH \quad (13)$$
(2-methyl-1-pentanol, b. p. 146–147° C.)

Table II shows that the alcohol boiling at 153–158° C. is the heptyl alcohol—2,4-dimethyl-1-pentanol. Reaction 11 therefore does not occur.

The alcohol boiling at 145–7° C. was identified as 2-methyl-1-pentanol, the product of Reaction 13. Reaction 12 therefore does not occur.

It will be noted that Reactions 11 and 12, which do not occur, involve loss of hydrogen from a CH_3 group, which is unlikely according to hypothesis (3).

To explain the formation of heptyl alcohols, one may write the following reactions on the basis of the known alcohols through hexyl. These are the only reactions which can be written between the various constituents in accordance with the tentative hypotheses:

$$CH_3CH_2CH_2CH(CH_3)CH_2OH + HCH_2OH \longrightarrow CH_3CH_2CH_2CH(CH_3)CH_2CH_2OH \quad (14)$$
(3-methyl-1-hexanol, b. p. about 165° C.)

$$CH_3CH_2CH(CH_3)CH_2OH + HCH_2CH_2OH \longrightarrow CH_3CH_2CH(CH_3)CH_2CH_2CH_2OH \quad (15)$$
(4-methyl-1-hexanol, b. p. 165° C.)

$$CH_3CH(CH_3)CH_2OH + CH_3HCHCH_2OH \longrightarrow CH_3CH(CH_3)CH_2CH(CH_3)CH_2OH \quad (16)$$
(2,4-dimethyl-1-pentanol, b. p. about 155–161° C.)

Table II shows that the alcohol, boiling at 162–164° C., is 4-methyl-1-hexanol and not 3-methyl-1-hexanol, which is unknown, but which would boil at about the same place. Reaction 14 seems therefore not to occur.

The identity of 2,4-dimethyl-1-pentanol was definitely established by comparison with synthetic material. This is the product of Reaction 16.

In the same manner, on the basis of the alcohols identified through heptyl, one may write the following reactions for the formation of octyl alcohols:

$$CH_3OH + CH_3CH_2CH(CH_3)CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH(CH_3)CH_2CH(CH_3)CH_2OH \quad (17)$$
(2,4-dimethyl-1-hexanol, b. p. about 175–178° C.)

$$CH_3CH_2CH(CH_3)CH_2CH_2CH_2OH + HCH_2OH \longrightarrow CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH_2OH \quad (18)$$
(5-methyl-1-heptanol, b. p. about 180–185° C.)

$$CH_3CH(CH_3)CH_2CH(CH_3)CH_2OH + HCH_2OH \longrightarrow CH_3CH(CH_3)CH_2CH(CH_2)CH_2CH_2OH \quad (19)$$
(3,5-dimethyl-1-hexanol, b. p. about 175–180° C.)

$$CH_3CH_2CH_2CH(CH_3)CH_2OH + HCH_2CH_2OH \longrightarrow CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_2OH \quad (20)$$
(4-methyl-1-heptanol, b. p. 182.7° C.)

$$CH_3CH_2CH(CH_3)CH_2OH + CH_3HCHCH_2OH \longrightarrow CH_3CH_2CH(CH_3)CH_2CH(CH_3)CH_2OH \quad (21)$$
(2,4-dimethyl-1-hexanol, b. p. about 175–180° C.

As can be seen from Table II, neither of the octyl alcohols was definitely identified. Both Reactions 17 and 21 seem more likely than 19, and, since they both give 2,4-dimethyl-1-hexanol, this structure is assigned to the compound boiling at 173–175° C.

Possibly Reaction 20 is more likely than 18, although insufficient evidence is at hand to choose between 4- and 5-methyl-1-heptanol.

Formation of Secondary Alcohols

It has thus been possible by means of the three simple dehydration hypotheses to account for the formation of all of the primary alcohols which have been found. In order to explain the formation of secondary alcohols, it is necessary only to extend these hypotheses to include a dehydration involving a hydrogen atom on the carbon atom holding the hydroxyl group (alpha condensation). As had been done for the primary alcohols, all of the reactions were written which could take place by such alpha condensations between the various primary alcohols, known to be present, and the secondary alcohols formed thereby. It was assumed that secondary alcohols would react always by loss of hydroxyl and not by loss of hydrogen. The first reaction would, of course, be that between methanol and ethyl alcohol to give isopropanol. While the series of reactions is not presented here, there is given in Table IV a list of the compounds which might be expected through the heptyl alcohols.

Table IV—Possible Secondary Alcohols

Substance	Boiling Point °C.
Isopropanol	82
sec-Butanol	99.5
3-Methyl-2-butanol	112.5
3-Pentanol	117
2-Pentanol	119
2-Methyl-3-pentanol	127
3-Methyl-2-pentanol	134
2,4-Dimethyl-3-pentanol	139
3,4-Dimethyl-2-pentanol	...
5-Methyl-3-hexanol	147–8
3-Ethyl-2-pentanol	148–152
3-Methyl-2-hexanol	160

It would also be possible to obtain a number of primary alcohols through dehydration between the hydroxyl groups of these secondary alcohols and hydrogen atoms on the beta-carbon of the other known primary alcohols. When these reactions were written, it was found either that the products called for could as well be explained by Reactions 1 to 16, or that the reactions involved a loss of hydrogen from a methyl group—a process which does not readily occur.

As outlined in Part I, the secondary alcohols—isopropanol, 3-methyl-2-butanol, and 2,4-dimethyl-3-pentanol—are definitely identified, while strong evidence is obtained for the presence of 3-pentanol, 2-pentanol, and 2-methyl-3-pentanol, which are six of the eight possible alcohols boiling within the range investigated. Again, the simple dehydration hypotheses explain the formation of the alcohols actually identified. It is probable that the other substances in Table IV exist in fractions which have not been investigated in sufficient detail for exact identification.

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